

# Uncertainty in A Priori Kinetics Predictions

**Stephen J. Klippenstein**

# Background

Uncertainties Playing a Major Role in Combustion Modeling  
Model Optimization **Hai Wang, Michael Frenklach, Tamas Turanyi**

Find feasible set of models that reproduce wideranging data  
=> reduced uncertainties in prediction space

Multiscale Optimization **Michael Burke**

Jointly optimize theoretical parameters, direct observables, global observables and elementary rate data. Yields best possible rate prescriptions

Global Uncertainty Studies **Tomlin, Davis, Skodje**

Use uncertainty & sensitivity to determine which rate coefficients to improve

Can use to optimize model outside range of observables via theoretical predictions of key rate coefficients



# Ab Initio Transition State Theory

$$k^{TST}(T) = \kappa \frac{k_B T}{h} \frac{Q^\#(T)}{Q_{reac}(T)} \exp\left(-\frac{E^\#}{k_B T}\right)$$

↓      ↓  
Tunneling Factor      Barrier Height – Saddle Point  
Close to 1      Rate Coefficient  
↑      ↑  
Rate Coefficient      Partition Functions – Depend on Rovibrational Properties



# Understand and Reduce Uncertainties in Elementary Rate Coefficient Predictions

- Electronic Energies Bill Green
- Vibrational Frequencies
- Torsional Modes Don Truhlar
- Energy Transfer Ahren Jasper/Jim Miller
- Large Esters Emily Carter



# Accurate Thermochemistry

Branko Ruscic

Active ThermoChemical Tables (ATcT)

Link together all measurements and solve to obtain self-consistent set of thermochemical data

Truly impressive accuracy – < 0.1 kcal/mol for many species

Ab Initio Thermochemistry

Long time effort to achieve chemical accuracy ~ 1 kcal/mol

Gn; CBS-QB3; G2M

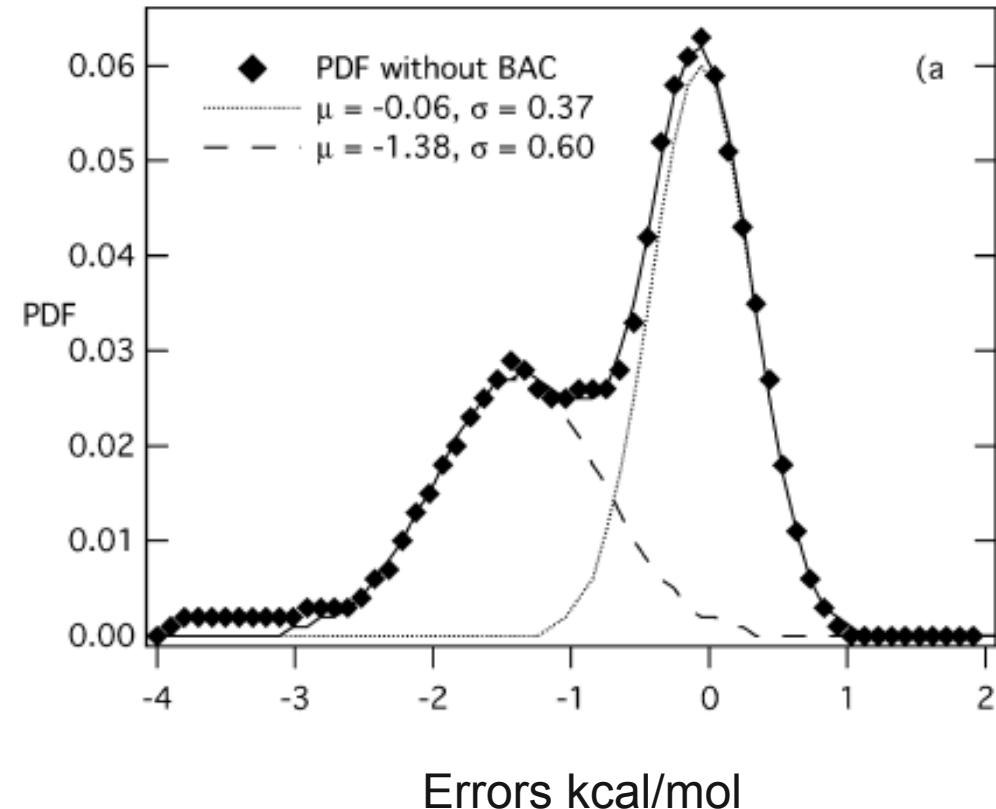
Approximations to CCSD(T)/CBS



# Combustion Thermochemistry Database

C. F. Goldsmith, G. R.  
Magoon, W. H. Green,  
J. Phys. Chem. A,  
(2012).

RQCISD(T)/CBS//  
B3LYP/6-311++G(d,p)



# Combustion Thermochemistry Database

RQCISD(T)/CBS//B3LYP/6-311++G(d,p)

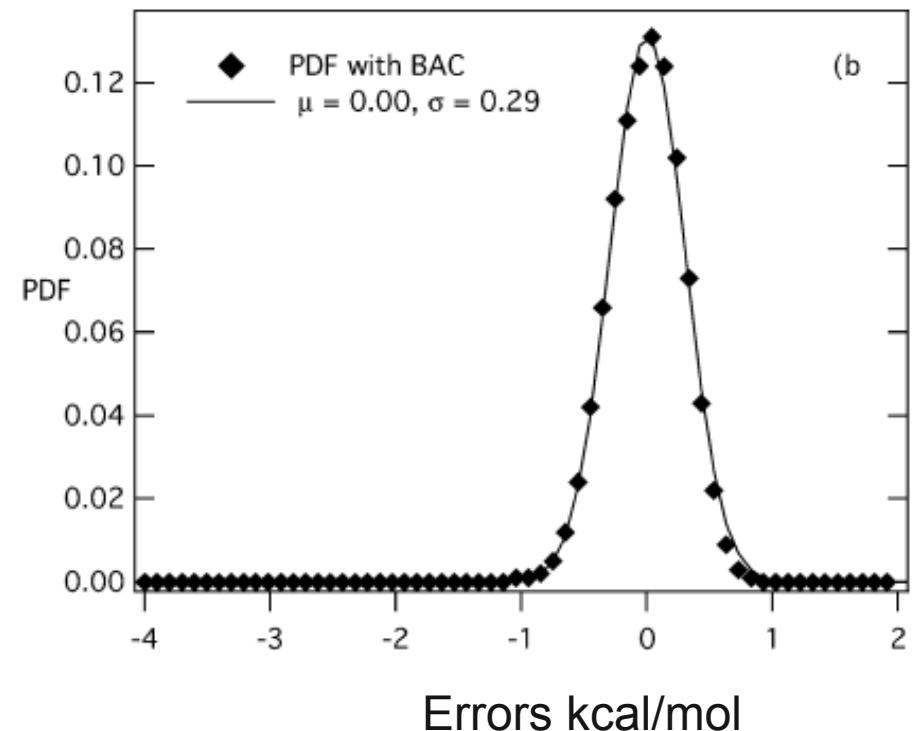
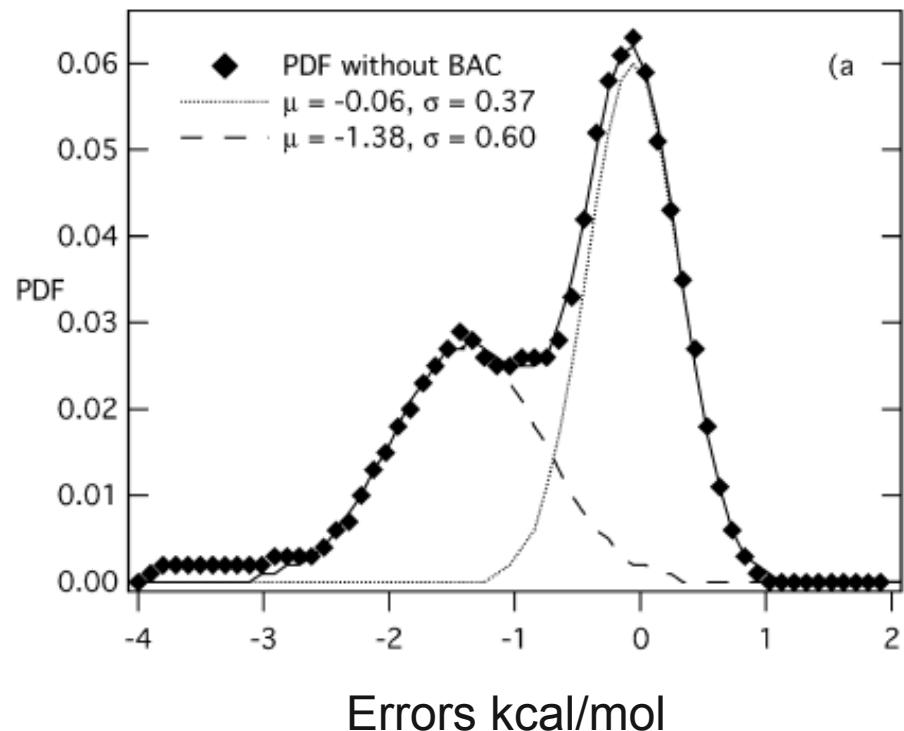
Need large basis set RQCISD(T) to get reliable treatment of TS

	bond type	correction [kcal/mol]
C. F. Goldsmith, G. R. Magoon, W. H. Green, J. Phys. Chem. A, (2012)	C—H	-0.03
Bond Additivity Correction	C—C	-0.36
Melius BAC-MP4	C=C	-0.96
	C≡C	-1.41
	O—H	0.21
	C—O	0.09
	C=O	0.11
	O—O	-0.58

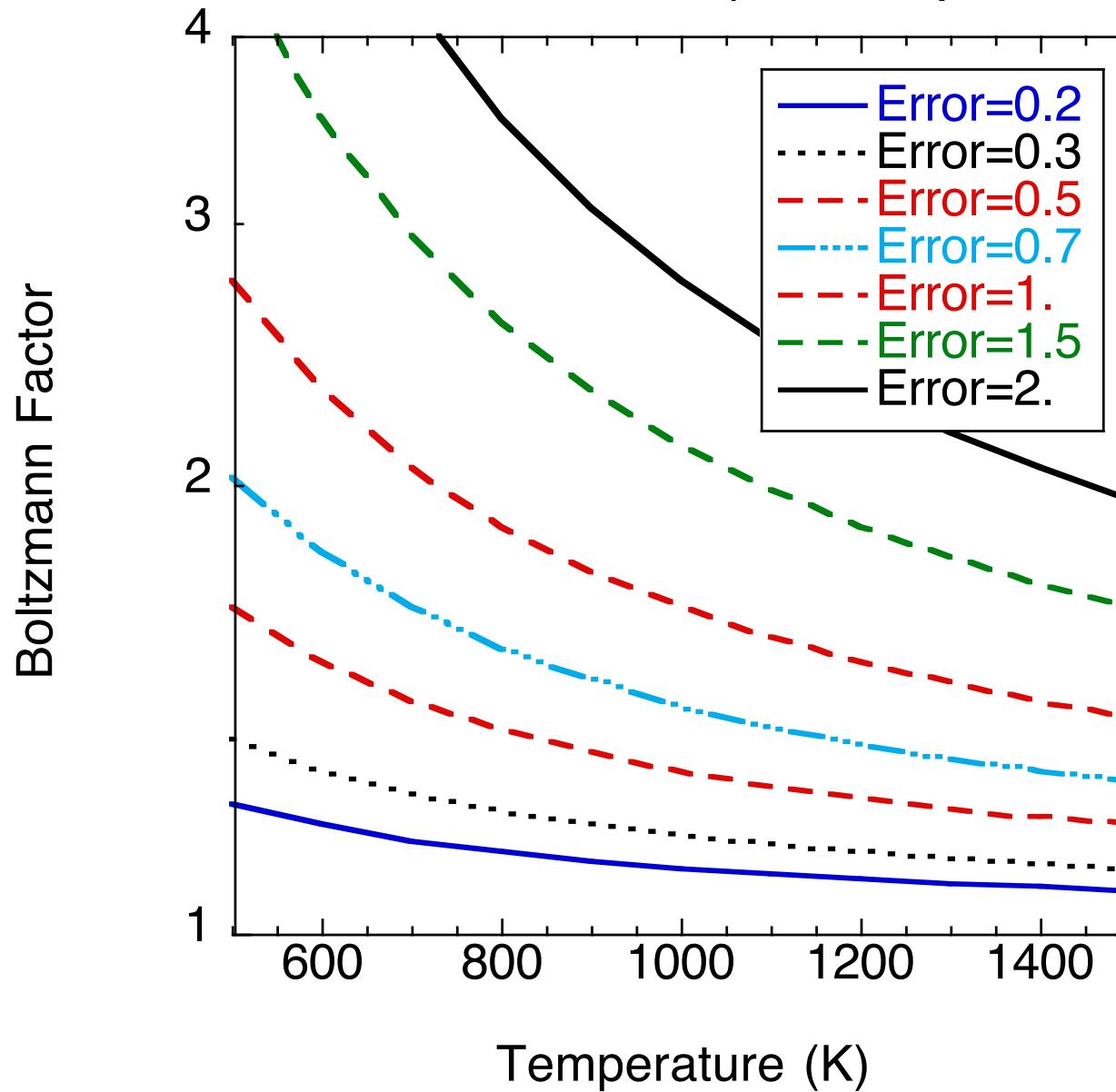


# Combustion Thermochemistry Database

$3 \sigma = 0.9 \text{ kcal/mol}$



# Boltzmann Uncertainties



What  
about  
TSs?



# High Accuracy Theoretical Methods

**W4** A. Karton, S. Doan, J. M. L. Martin, Chem. Phys. Letts., 510, 165-178 (2011); A. Barton, E. Rabinovich, J. M. L. Martin, B. Ruscic, J. Chem. Phys. 125, 144108 (2006).

**HEAT** M. E. Harding, J. Vazquez, B. Ruscic, A. K. Wilson, J. Gauss, J. F. Stanton, J. Chem. Phys. 128, 114111 (2008).

**Focal Point** (Allen and coworkers)

Current Best  $\sigma \sim 0.1$  kcal/mol



# Combustion Thermochemistry Database

CCSD(T)/TZ optimizations and Frequencies

CCSD(T)/CBS from CCSD(T)/AQZ',A5Z'

CCSDT(Q)/DZ

Core-Valence CCSD(T)/CBS; TZ and QZ

Relativistic from DKH with CI/TZ

DBOC from HF/cc-pVTZ

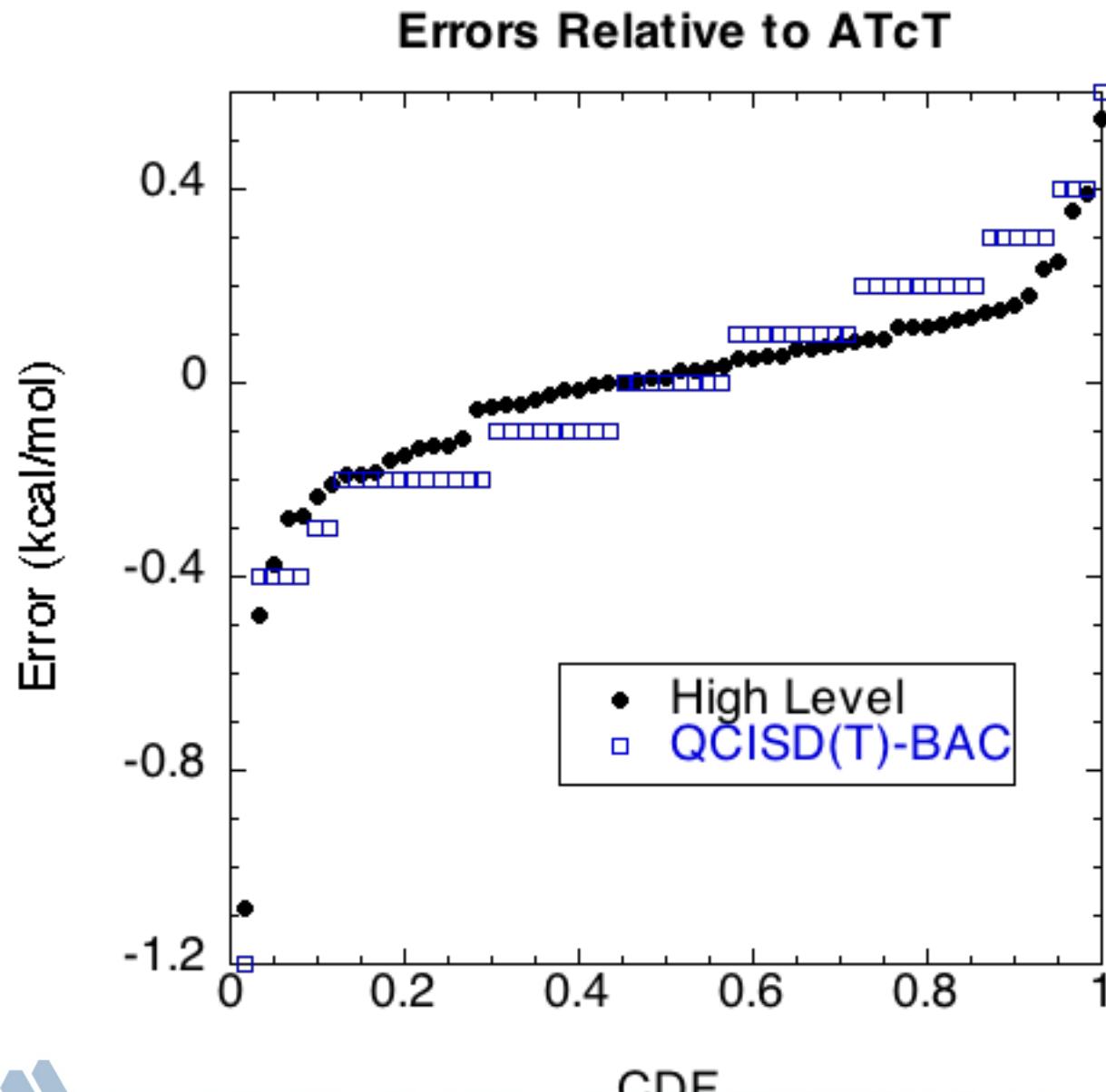
Anharmonic corrections from B3LYP/6-311++G\*\*

Heats of formation relative to H<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, NH<sub>3</sub>

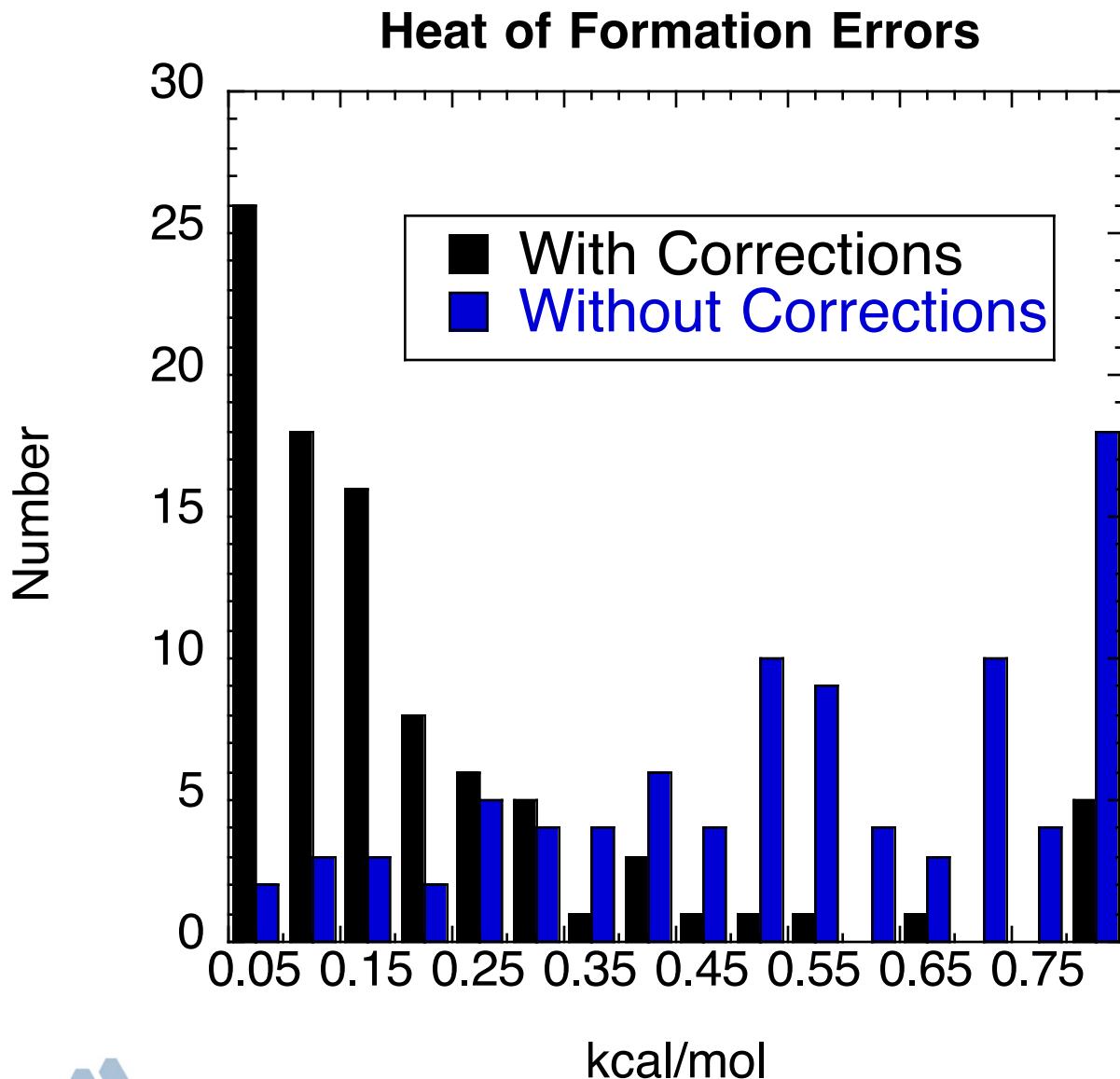
5 Heavy Atoms



# Errors in High Level Method



# Accuracy vs ATcT from Ruscic



H, O, OH, O<sub>2</sub>, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, C, CH, CH<sub>2</sub>, 1CH<sub>2</sub>, CH<sub>3</sub>, CO, HCO, COH, CH<sub>2</sub>O, HCOH, CH<sub>2</sub>OH, CH<sub>3</sub>O, CO<sub>2</sub>, HOCO, HCO<sub>2</sub>, OCHOH, CH<sub>3</sub>O<sub>2</sub>, CH<sub>3</sub>OOH, C<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>CC, C<sub>2</sub>H<sub>3</sub>, CCH<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>, CHCH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>6</sub>, CCO, 1CCO, HCCO, CH<sub>2</sub>CO, HCCOH, CH<sub>3</sub>CO, CH<sub>3</sub>CHO, CH<sub>2</sub>CHOH, CH<sub>3</sub>CHOH, C<sub>2</sub>H<sub>4</sub>OH, CH<sub>3</sub>CH<sub>2</sub>O, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>OCH<sub>3</sub>, OCHCHO, CH<sub>3</sub>C(O)OH, CH<sub>2</sub>CCH, CH<sub>3</sub>CCH, CH<sub>2</sub>CCH<sub>2</sub>, -CH<sub>2</sub>CHCH-, CH<sub>3</sub>CHCH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>, N, NNH, NHNN, H<sub>2</sub>NN, NHNNH<sub>2</sub>, NH<sub>2</sub>NH<sub>2</sub>, NO, HNO, NOH, H<sub>2</sub>NO, HNOH, H<sub>2</sub>NOH, N<sub>2</sub>O, NO<sub>2</sub>, NO<sub>3</sub>, CN, HCN, CNH, H<sub>2</sub>CN, HCNH, CH<sub>3</sub>N, CH<sub>2</sub>NH, CH<sub>3</sub>NH, CH<sub>2</sub>NH<sub>2</sub>, CH<sub>3</sub>NH<sub>2</sub>, NCO, HNCO, HCNO, NCOH

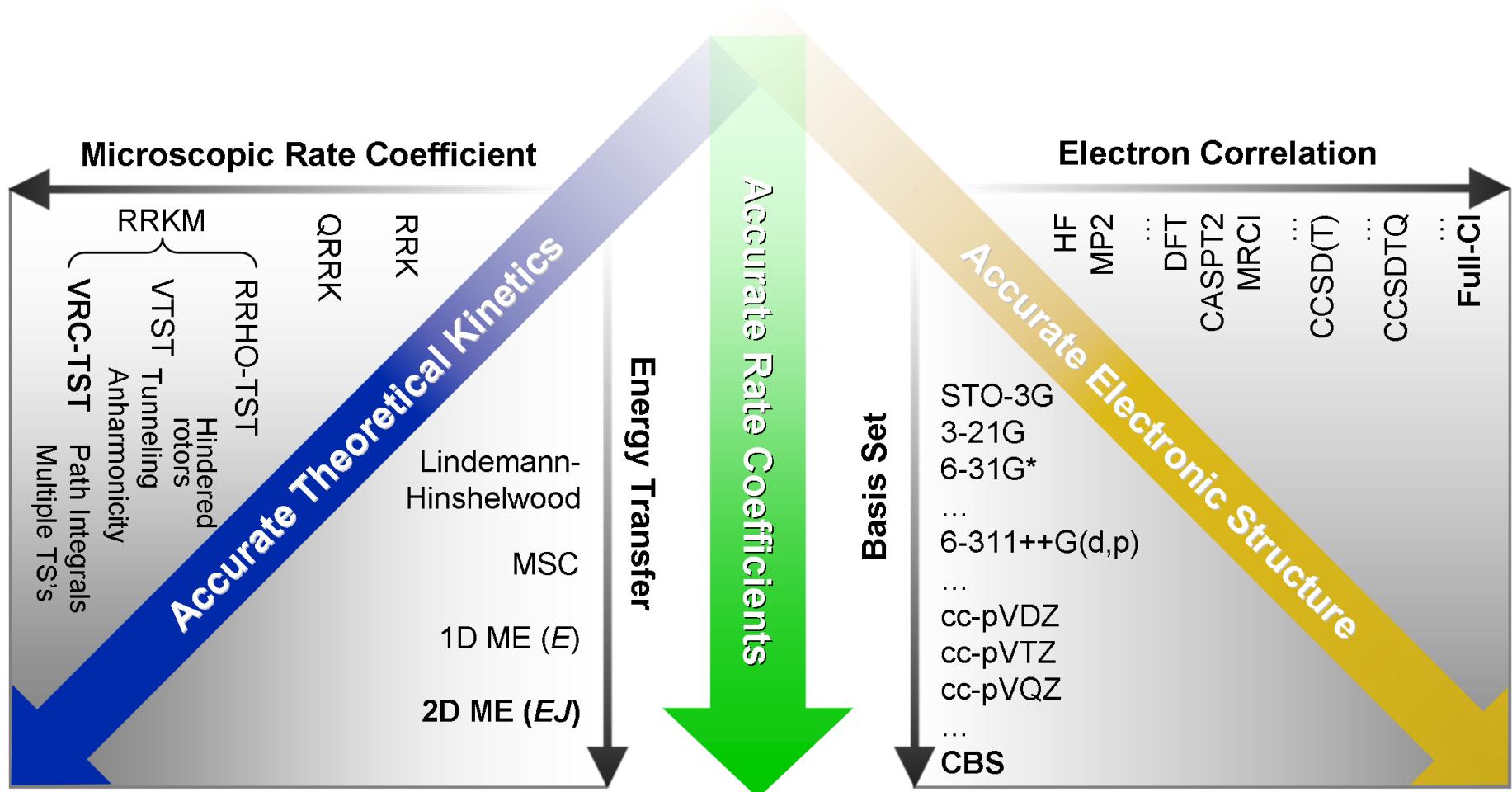


# Size of Individual Corrections

	Mean	MAD	RMSD	Variance
CCSDT(Q)	-0.36	0.42	0.62	0.46
Core-Valence	0.54	0.54	0.60	0.28
Anharmonicity	0.47	0.49	0.59	0.32
Relativistic	-0.16	0.16	0.20	0.11
DBOC	0.10	0.11	0.14	0.09



# Errors from Electronic Structure & Kinetic Theory Approximations Should be Comparable



J. Zador



# Rovibrational Properties Reactions on C<sub>2</sub>H<sub>5</sub> PES

Product of CCSD(T) frequencies for  
specified basis relative to CCSD(T)/CBS

Stationary Point	DZ	TZ	QZ	ADZ
C <sub>2</sub> H <sub>5</sub>	1.081	1.030	1.012	0.851
C <sub>2</sub> H <sub>4</sub> +H=C <sub>2</sub> H <sub>5</sub>	0.905	0.909	0.962	0.838
C <sub>2</sub> H <sub>5</sub> ;TAU	0.840	1.020	1.008	0.868
C <sub>2</sub> H <sub>5</sub> =C <sub>2</sub> H <sub>5</sub>	0.881	1.004	1.002	0.821
H+C <sub>2</sub> H <sub>4</sub> =C <sub>2</sub> H <sub>3</sub> +H <sub>2</sub>	0.984	1.130	1.052	0.996
C <sub>2</sub> H <sub>4</sub> +H	0.896	0.984	0.993	0.876
C <sub>2</sub> H <sub>3</sub> +H <sub>2</sub>	0.945	1.003	1.001	0.908



# Rovibrational Properties Reactions on C<sub>2</sub>H<sub>5</sub> PES

Product of frequencies for specified method  
relative to CCSD(T)/CBS

Stationary Point	B3LYP 6-311++G**	M06-2X 6-311++G**	RMP2 TZ	UMP2 TZ
C2H5	0.723	0.759	1.210	1.300
C2H4+H=C2H5	0.493	1.085	1.558	2.274
C2H5;TAU	0.992	0.953	1.289	1.179
C2H5=C2H5	0.988	1.097	1.219	1.355
H+C2H4=C2H3+H2	1.183	1.103	0.621	2.518
C2H4	1.034	1.186	1.144	1.144
C2H3+H2	0.966	1.181	1.170	1.937



# Rovibrational Properties Reactions on C<sub>2</sub>H<sub>5</sub> PES

Product of frequencies for specified method  
relative to CCSD(T)/CBS

Stationary Point	CAS+1+2 TZ	CAS+1+2+QC TZ	CASPT2 TZ	CCSD(T)/DZ+ MP2/TZ-MP2/DZ
C2H5	1.550	1.124	1.162	0.983
C2H4+H=C2H5	1.375	1.013	0.863	0.900
C2H5;TAU	1.350	1.104	1.309	1.046
C2H5=C2H5	1.396	1.104	1.119	0.964
H+C2H4=C2H3+H2	1.570	1.199	1.049	1.077
C2H4	1.386	1.180	1.115	0.953
C2H3+H2	1.241	1.048	1.079	0.974



# Rovibrational Properties Reactions on C<sub>2</sub>H<sub>5</sub> PES

Energy errors for high level calculations at CCSD(T) geometry with specified basis set relative to calculations at CCSD(T)/CBS geometry

Stationary Point	DZ	TZ	QZ	ADZ
C2H5	0.000	0.000	0.000	0.000
C2H4+H=C2H5	-0.061	-0.067	-0.028	0.157
C2H5;TAU	-0.059	0.050	0.020	0.044
C2H5=C2H5	-0.029	0.045	0.018	-0.008
H+C2H4=C2H3+H2	0.229	0.132	0.054	0.510
C2H4	-0.003	-0.007	-0.003	0.235
C2H3+H2	0.228	0.048	0.020	0.417



# Rovibrational Properties Reactions on C<sub>2</sub>H<sub>5</sub> PES

Energy errors for high level calculations at geometry  
with specified method relative to calculations at  
CCSD(T)/CBS geometry

Stationary Point	B3LYP 6-311++G**	M06-2X 6-311++G**	RMP2 TZ	UMP2 TZ
C2H5	0.000	0.000	0.000	0.000
C2H4+H=C2H5	-0.587	0.265	-0.792	0.511
C2H5;TAU	0.100	0.101	0.077	0.011
C2H5=C2H5	0.178	0.234	0.013	0.298
H+C2H4=C2H3+H2	0.564	0.115	-0.571	1.932
C2H4	0.264	0.382	-0.154	-0.181
C2H3+H2	0.239	0.435	0.011	1.479



# Rovibrational Properties Reactions on C<sub>2</sub>H<sub>5</sub> PES

Energy errors for high level calculations at geometry  
with specified method relative to calculations at  
CCSD(T)/CBS geometry

Stationary Point	CAS+1+2 TZ	CAS+1+2+QC TZ	CASPT2 TZ	CCSD(T)/DZ+ MP2/TZ-MP2/DZ
C2H5	0.000	0.000	0.000	0.000
C2H4+H=C2H5	-0.310	-0.570	<b>-0.510</b>	<b>-0.111</b>
C2H5;TAU	<b>-0.007</b>	<b>-0.413</b>	<b>-0.103</b>	0.058
C2H5=C2H5	-0.149	-0.448	-0.306	-0.012
H+C2H4=C2H3+H2	-0.207	<b>-0.817</b>	-0.296	<b>0.105</b>
C2H4	<b>-0.335</b>	-0.447	-0.501	-0.052
C2H3+H2	-0.320	-0.540	-0.347	0.026



# Rovibrational Properties Reactions on CH<sub>3</sub>O PES

Product of frequencies for CCSD(T) calculations with specified basis set relative to CCSD(T)/CBS

Stationary Point	DZ	TZ	QZ	ADZ
CH3O	1.14	1.10	1.04	0.93
CH2OH	1.31	1.10	1.04	0.97
CH2OH;PERP	1.06	1.01	1.00	0.97
CH2OH;PLAN	0.97	1.01	1.00	0.88
CH3O=CH2OH	0.95	1.02	1.01	0.87
H+H2CO=HCO+H2	1.11	1.11	1.04	1.04
CH2OH=H2CO+H	0.57	0.76	0.90	0.93
CH3O=H+H2CO	1.06	1.00	1.00	0.97
4CH3+O=CH2+OH	0.61	0.96	0.99	0.96
CH+H2O=CH2OH	1.19	1.12	1.05	0.77
CH+H2O=CH2OH;TAU	1.02	1.08	1.03	0.83
4CH+H2O=CH2+OH	1.68	1.27	1.11	0.84
H+H2CO	0.98	1.00	1.00	0.92
HCOH+H	0.97	1.00	1.00	0.89
HCOH+H;TRANS	0.99	0.99	1.00	0.91
H2+HCO	0.97	1.00	1.00	0.93
H2+HOC	0.99	1.00	1.00	0.93
CH+H2O	0.99	1.00	1.00	0.95
CH3+O	0.77	0.97	0.99	0.94
CH2+OH	1.01	1.00	1.00	
HCOH+H=HCO+H2;CIS	1.21	1.18	1.07	0.86
HCOH+H=HCO+H2;TRANS	1.03	1.03	1.01	0.84
HCOH+H=HOC+H2;CIS	1.22	1.24	1.10	0.80
HCOH+H=HOC+H2;TRANS	1.03	0.93	0.97	0.90



# Rovibrational Properties Reactions on CH<sub>3</sub>O PES

Product of frequencies for specified method relative to CCSD(T)/CBS

Stationary Point	B3LYP 6-311++G**	M06-2X 6-311++G**	RMP2 TZ	UMP2 TZ
CH3O	0.85	1.34	1.35	1.35
CH2OH	0.84	1.00	1.01	1.25
CH2OH;PERP	0.90	1.04	0.89	1.16
CH2OH;PLAN	0.96	0.94	1.11	1.10
CH3O=CH2OH	0.89	1.15	1.50	1.35
H+H2CO=HCO+H2	1.33	1.43	1.35	1.69
CH2OH=H2CO+H	0.54	0.84	2.30	2.48
CH3O=H+H2CO	0.60	0.92	1.43	1.75
4CH3+O=CH2+OH	0.95	0.35	1.26	1.34
CH+H2O=CH2OH	0.91	1.46	1.30	1.24
CH+H2O=CH2OH;TAU	0.83	1.61	1.13	0.97
4CH+H2O=CH2+OH	0.96	1.27	-0.69	1.34
H+H2CO	0.98	1.12	1.05	1.05
HCOH+H	0.91	1.07	1.11	1.11
HCOH+H;TRANS	0.98	1.11	1.08	1.08
H2+HCO	0.99	1.07	1.01	1.07
H2+HOC	0.91	1.04	1.06	1.06
CH+H2O	0.94	1.00	1.04	1.04
CH3+O	1.00	0.96	1.09	1.03
CH2+OH	0.93	1.05	1.10	1.11
HCOH+H=HCO+H2;CIS		0.75	1.31	2.10
HCOH+H=HCO+H2;TRANS		0.95	1.24	2.22
HCOH+H=HOC+H2;CIS		1.33	2.17	3.11
HCOH+H=HOC+H2;TRANS		1.21	1.75	6.48



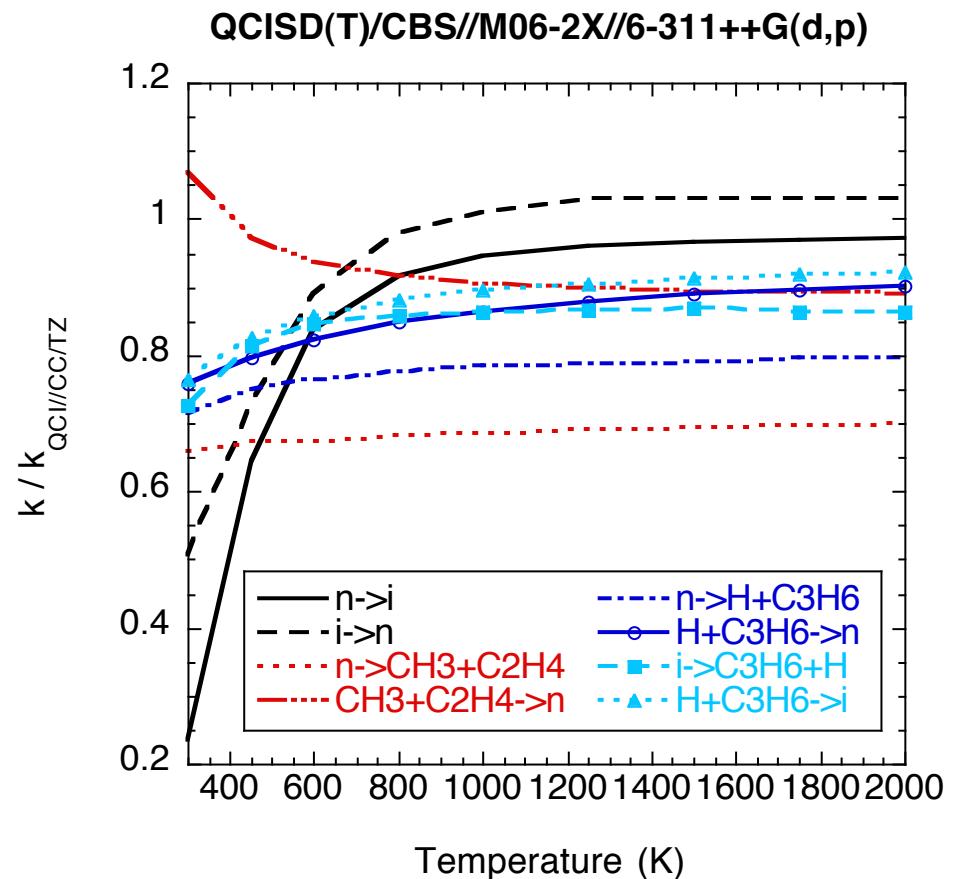
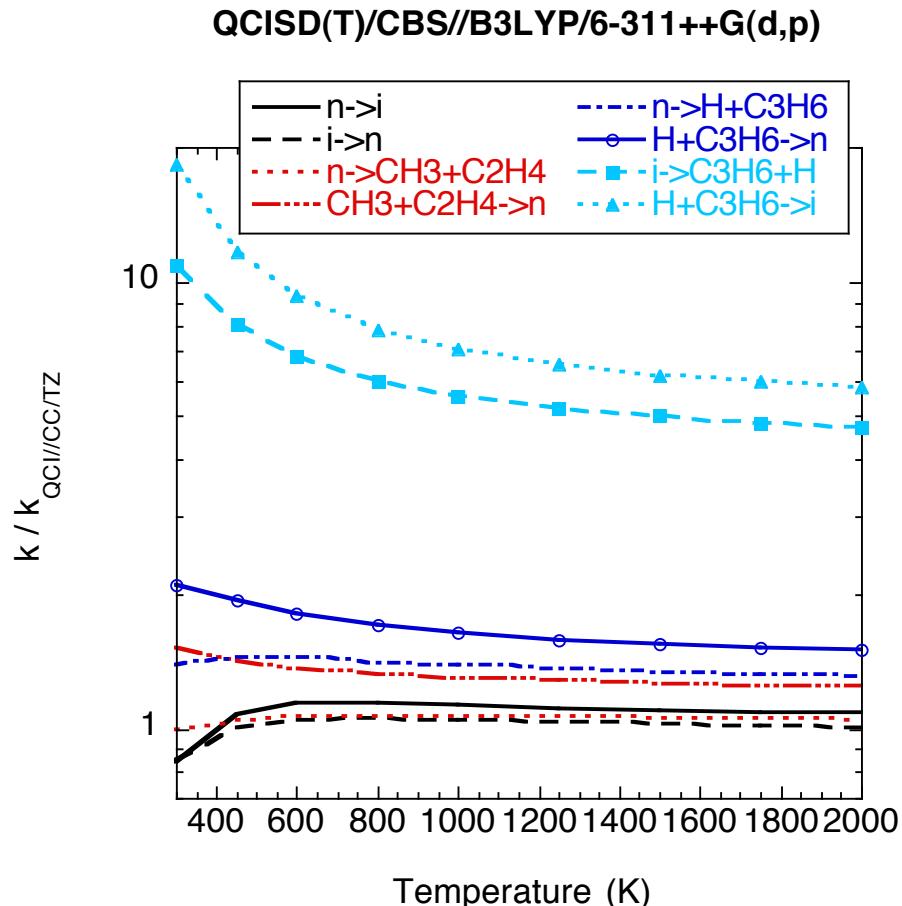
# Rovibrational Properties Reactions on CH<sub>3</sub>O PES

Product of frequencies for specified method relative to CCSD(T)/CBS

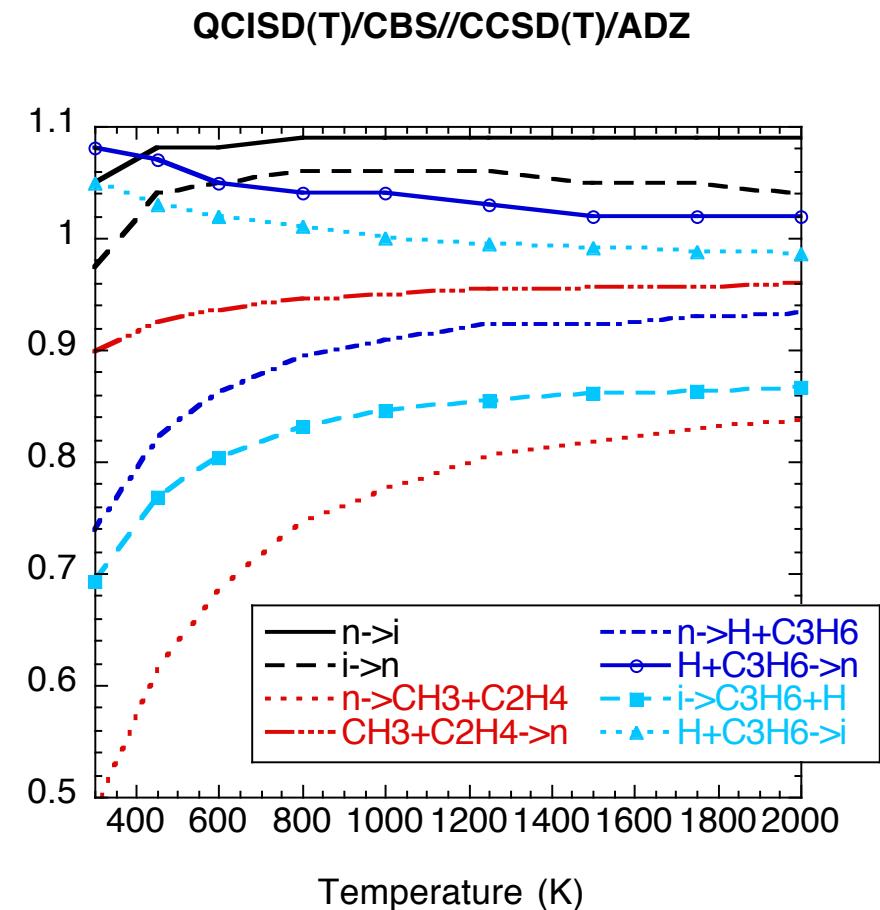
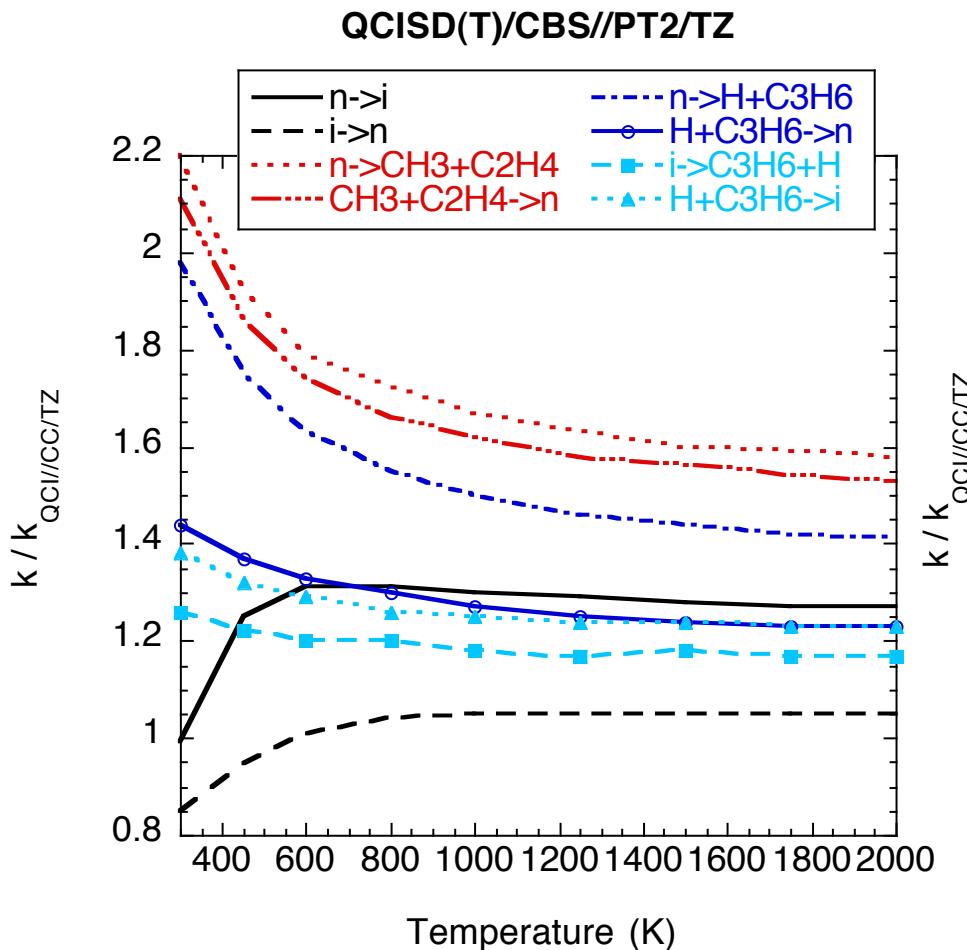
Stationary Point	CAS+1+2 TZ	CAS+1+2+QC TZ	CASPT2	CCSD(T)/DZ+ MP2/TZ- DZ
CH3O	1.58	1.26	1.33	1.13
CH2OH	1.40	1.14	0.94	1.00
CH2OH;PERP	1.36	1.06	0.88	0.91
CH2OH;PLAN	1.15	1.04	1.17	0.98
CH3O=CH2OH	1.52	1.18	1.51	0.95
H+H2CO=HCO+H2	1.75	1.39	1.37	1.06
CH2OH=H2CO+H	3.26	2.38	2.39	0.71
CH3O=H+H2CO	1.99	1.39	1.20	1.00
4CH3+O=CH2+OH				0.96
CH+H2O=CH2OH				0.99
CH+H2O=CH2OH;TAU				0.95
4CH+H2O=CH2+OH				1.22
H+H2CO	1.26	1.08	1.06	0.99
HCOH+H	1.25	1.08	0.70	0.98
HCOH+H;TRANS	1.22	1.06	0.44	0.98
H2+HCO				0.99
H2+HOC				0.98
CH+H2O				0.99
CH3+O				1.01
CH2+OH				0.99
HCOH+H=HCO+H2;CIS	2.42	1.47	1.66	1.13
HCOH+H=HCO+H2;TRANS	1.66	1.24	1.20	0.94
HCOH+H=HOC+H2;CIS	2.45	1.97	1.92	1.19
HCOH+H=HOC+H2;TRANS	1.84	1.48	1.37	0.98



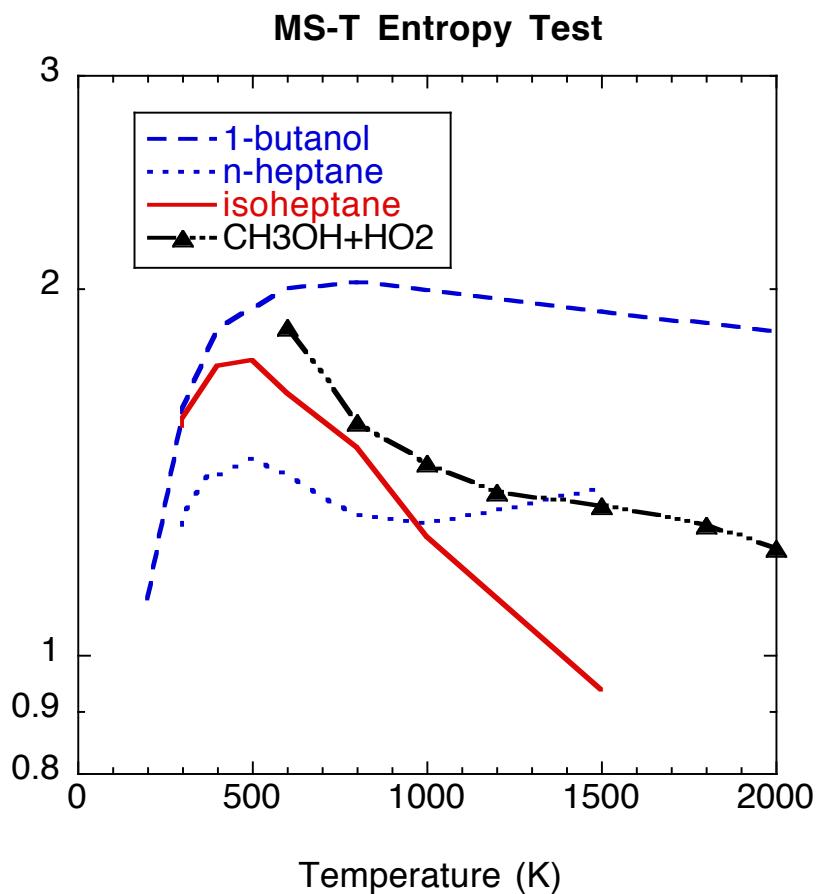
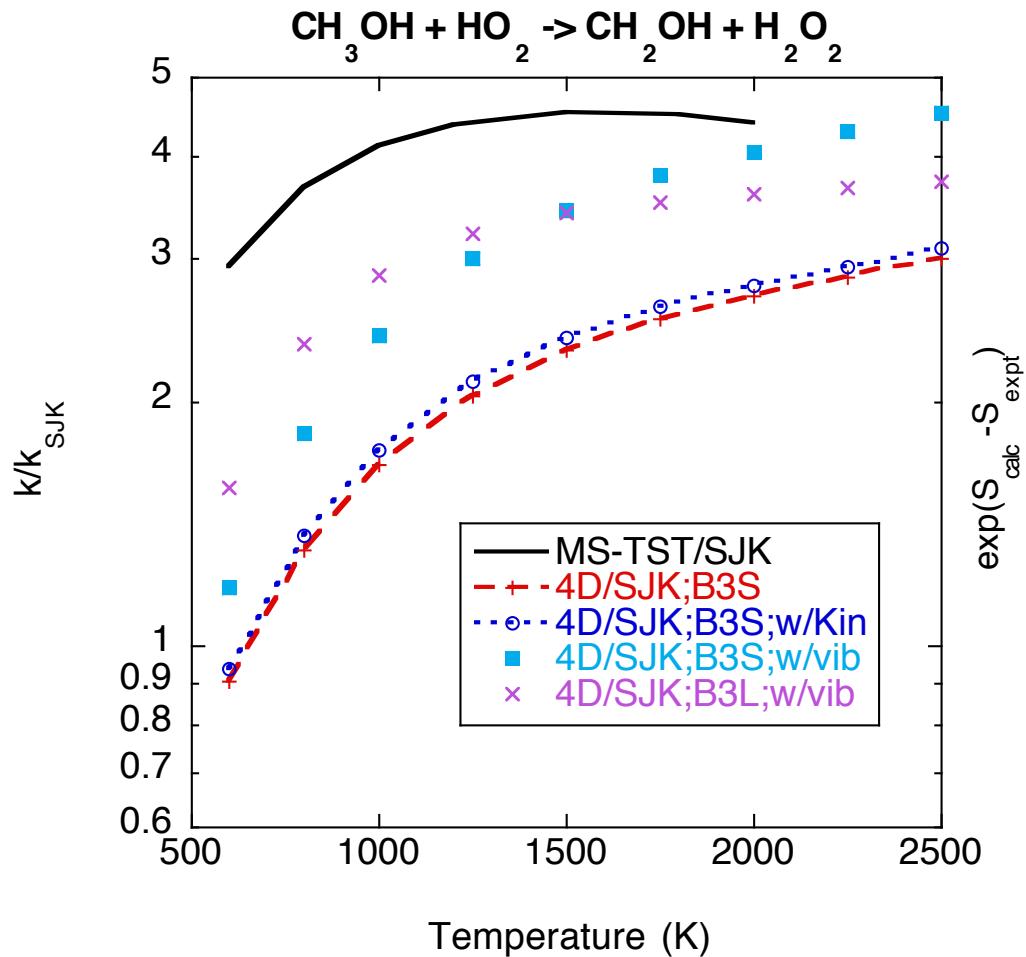
# Rovibrational Properties Reactions on C<sub>3</sub>H<sub>7</sub> PES



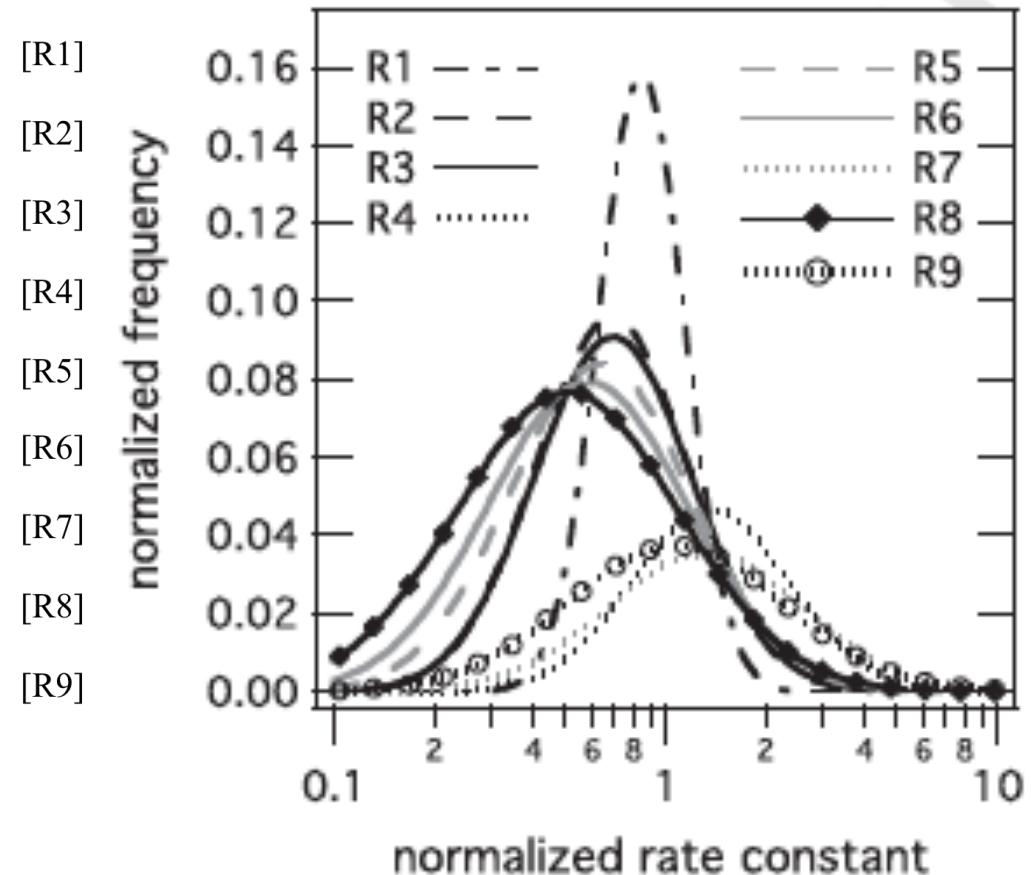
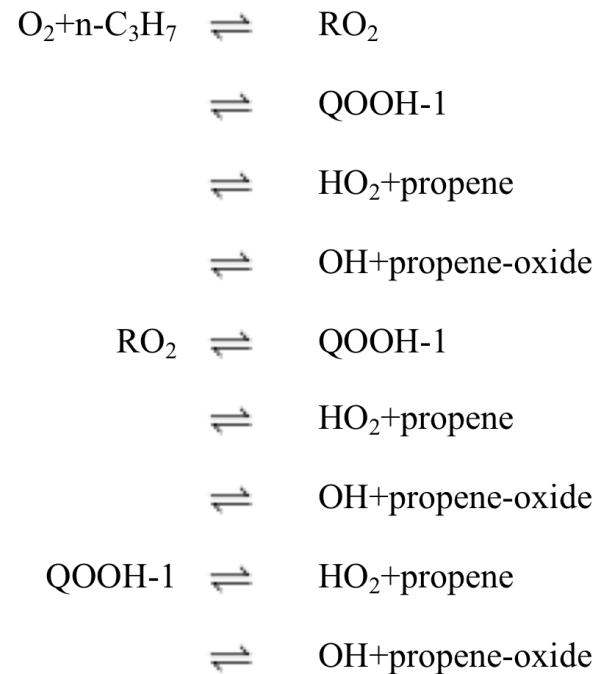
# Rovibrational Properties



# Direct Sampling of Torsions



# Coupling of Uncertainties: n-propyl + O<sub>2</sub>



C. F. Goldsmith, A. S. Tomlin, S. J. Klippenstein, Proc. Comb. Inst. 34, in press (2012)



# Funding

## US-Department Of Energy

1. Combustion Energy Frontier Research Center
2. Chemical-Physics Program – Chemical Dynamics in the Gas Phase Group
3. Argonne-Sandia Consortium on High Pressure Combustion Chemistry

## Summary

- High level energies have  $1\sigma$  uncertainties of ~0.1-0.2 kcal/mol
- Traditional approaches to determining vibrational properties contribute factor of two or more to uncertainties

